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"EFFECT OF ATOMIC RADIATION ON THE
COMBUSTION OF HYDROCARBON AIR MIXTURES"

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The effect of nuclear radiation on combustion of hydrocarbon-air flames has been experimentally investigated from a phenomenological standpoint. No attempt was made to obtain kinetic data, but it will be shown that the results obtained are consistent with proposed mechanisms for flame propagation and the interaction of radiation and matter. It was demonstrated that the combustion effectiveness is increased by a strong source of radiation in the vicinity of the radiation zone.

Introduction

Soon after the discovery, in the early twentieth century, of the nature of the radiation from radioactive material, considerable interest was shown in the effect such radiation would have on various chemical systems. Lind, in 1921 published the first edition of a monograph entitled "The Chemical Effects of Alpha Particles and Electrons" (American Chemical Society Monograph Number 2) in which he discusses theoretical and experimental contributions to this field.⁵ In particular, it is shown that gaseous hydrocarbons may be altered by the absorption of energy from radioactive materials.

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The possibility of utilizing radioactive materials to increase reaction rates was not seriously considered until more recent years.

As a result of the operation of this nation's atomic energy program, there resulted an accumulation of quantities of radioactive materials, called fission products. These isotopes are essentially the "ashes" resulting from the fission of uranium fuel in nuclear reactors. In an attempt to find uses for these materials, the United States Atomic Energy Commission has sponsored research to survey aspects of fission product utilization.

The possible improvement of power plant operation by the introduction of radioactive sources into the combustion phase is one such possible use. In view of these possible improvements, the effect of beta emitting radioactive source on Bunsen and drag stabilized flames has been investigated (1, 2, 3).

Theory

The process of the absorption of beta radiation by a medium surrounding the radiation source has been treated from a theoretical standpoint. Spring¹⁰ offers a review of some of the proposed mechanism of these interactions, but calculations necessary to quantitatively evaluate the effect of the electrons on a chemical system are not readily performed. Lind⁵ has offered several working equations specifically derived for application to reacting systems, and suitable modification of these relationships will be employed.

The process of absorption of beta radiation may be described if one knows the energy of the particles and characteristics of the absorbing medium. Complicating factors which prevent an exact description are secondary radiation, reflection, and the distribution of the energy of beta radiation.

For particles of average energy of $10^5 - 10^6$ electron volts, attenuation takes place at a rate which is roughly inversely proportional to the density of the medium. As the electron passes through, it causes ionization of the attenuating medium along the electron's path. These resultant ions are formed in pairs, and consist of relatively large fragments of the original molecules. The potential for the formation of such a pair is approximately 33 electron volts, on the average.⁷ This value is in excess of usual values for activation energies. Existence of these pairs has been confirmed by cloud chamber and similar techniques.¹⁰ As the energy from the incident electrons is absorbed, the overall energy of the system is changed by adding to the original energy spectrum an additional distribution around 33 electron volts. This is shown schematically in Figure 1. It should be noted that this process does not cause significant alteration in the mean energy, as thermal radiation would.

If E_T is the activation energy, the net effect of the radiation is to increase the number of molecules of energy greater than E_T . It should be noted that some molecules may absorb energy without undergoing ionization.

A simple kinetic model may be devised by considering a reaction rate given by the equation

$$\frac{-dN_A}{dt} = k N_A^\alpha \quad (1)$$

and k is determined by the Arrhenius equation

$$k = A \exp [-E_T/RT] \quad (2)$$

where $\exp [-E_T/RT]$ is the fraction of molecules of energy equal to, or greater than E_T , for a normal distribution.⁴ However, for the case being considered, an additional fraction of molecules possess energy greater than E_T by virtue of the radiation absorption.

Let $y(\beta)$ be this additional fraction. The rate constant equation may then be modified to (approximately)

$$k^1 = A \exp(-E_T/RT) + y(\beta) \quad (3)$$

The value of $y(\beta)$ is a function of source strength, the source energy, the average life of the specie formed, absorption factors and geometry. Dividing equation (3) by (2) one obtains the ratio of reaction rates constants as

$$\frac{k^1}{k} = 1 + y(\beta) \exp(+E_T/RT) \quad (4)$$

To calculate $y(\beta)$ it is necessary to calculate the number of ion pairs formed. If N is the number of ion pairs formed, then

$$N = \frac{E\beta}{35} \times 3.7 \times 10^{16} \text{ ion pair/sec} \quad (5)$$

where E is the source strength in million electron volts, and β the activity in curies. The specific ionization is given by

$$N^1 = \frac{E\beta}{33R} \times 3.2 \times 10^{16} \text{ ion pair/sec/cm} \quad (6)$$

where R is the range of the electron in centimeters.

For system whose principal dimension, L , is less than R , and the source is located within the boundaries of the system, equation (6) must be modified to account for losses of radiation through the boundaries. A simple system of this type is a source in the wall of a hollow cylinder of diameter D equal length L . If electrons are emitted from points in the wall and travel along diameters to opposite points, the ionization induced will be

$$N_i = 3.7 \times 10^{16} \frac{E\beta L}{33R} \text{ ion pair/sec} \quad (7)$$

Upon reaching the opposite points, they will be either absorbed or reflected.

Those which are reflected will go through a similar process after being reflected. The maximum number of times any electron may be reflected is R/L . If F is the fraction of electrons reradiated, the total pair formation for a source of this type is

$$N_T = 3.7 \times 10^{16} \frac{E_{BL}}{33R} S_n \quad (8)$$

where S_n is the sum of the finite series

$$1 + F + F^2 + \dots + F^n \text{ where } F < 1$$

and n is the nearest integer less than R/L . The value of L is not a simple function of the physical dimensions of the system, but is an average length which may be calculated from consideration of the spatial distribution of the emitted electrons.

In the event several energies are associated with the particular decay process, it is necessary to evaluate the ionic contribution of each energy separately and then add the individual values. The effect of secondary radiation (Bremsstrahlung) is evaluated by similar techniques.

The value of $y(\beta)$ for a flow system is obtained from equation (8) by the equation

$$y(\beta) = 2 \theta \frac{N_T}{AM} \quad (9a)$$

$$\text{or} \quad y(\beta) = \frac{2 \theta E_{BL} S_n}{33AMR} \times 3.7 \times 10^{16} \quad (9b)$$

where M is the molal flow rate (moles per sec); A is the Avagadro number; θ is the ratio of the average life of an ion to the resident time in the system; and the factor 2 is proportionality factor for converting ion pairs to molecules. This equation applies to a single step process. For radiation induced chain reaction $y(\beta)$ must be multiplied by the average chain length. These equations serve as a guide for experimental design and are correct only to orders of magnitude.

The type of reactions induced by radiation are in many respects similar to combustion processes. Ozone has been identified in irradiated oxygen⁵ and may be formed as follows:

or

Organic fuels are subjected to a series of reactions which include bond splitting, dehydrogenation, and other rearrangements.⁵

For a saturated hydrocarbon

are two possible overall reactions. In particular, for propane, one may have propyl, ethyl and methyl radicals, free hydrogen, and charged particles.

Unsaturated hydrocarbons are even more reactive under radiation. Combination of the products of reaction (f) and (g) with those of reaction (a) - (e) will give various oxidation products of the hydrocarbons.⁵

Examination of equation (4) shows that the radiation induced reactions should be more pronounced in the preflame zone and that the overall effect is to introduce into the reaction volume highly reactive species, and to increase the total reaction time.

The isotopes used in these studies were palladium - 109, gold - 198, and copper - 64. Table I gives the characteristics of these materials.⁶

TABLE I

Characteristics of Radioactive Isotypes

Isotope	Half Life Hrs	Energy, Million Electron Volts			Maximum Act- ivity Curies
		β^-	B+	γ	
*Cu ⁶⁴	12.9	.55	.60	1.35	1300
Au ¹⁹⁸	65	.96	None	.41	2100
Pd ¹⁰⁹	14	.95	None	None	<100

* Cu⁶⁴ served as bond for Au¹⁹⁸

Equipment

The equipment used in this work is shown schematically in Figures 2, 3, and 4. It consisted of a Bunsen burner which could be surrounded by radioactive foil (Fig. (2)), a radioactive spherical flameholder placed at the exit of the Bunsen burner (Fig. (3)) and a constant-area combustion chamber of circular cross section with a flameholder (Fig. 4), the radioactive material being inserted in the walls.

In the first two series of runs, the Bunsen burner and spherical flameholder, Pd¹⁰⁹ was the source material. Since this isotope is a pure beta emitter, it was only necessary to use light shielding to protect the investigators. Handling was readily accomplished with tongs and other tools, 3 feet long. A vacuum chamber, fabricated of 3/8 in. steel, in which the burner was located, provided adequate shielding. For the final series of runs, utilizing the constant area combustor, Au¹⁹⁸ and Cu¹⁶⁴ were the source materials. Due to the rather high γ activity, it was necessary to design the equipment so that all assembly and data taking operations could be performed remotely. Figure 5 is a plan view of the experimental equipment and Figure 6 is a line

diagram of the instrumentation and control lines. Approximately 5 feet of water or 30 inches of sand were necessary to provide adequate shielding.*

The burner was constructed in several parts (Fig. 7). The burner tube was attached to the bottom of a 6-foot vertical tank (Fig. 8), and the tank filled with water. It was then possible to assemble the burner components under water by means of long tongs (Figs. 9, 10, 11, 12).

Additional safety precautions included the installation of a filter in the exhaust line from the plenum chamber, a blow-out diaphragm in tee on the exhaust line and water cooling in the burner head.

The flameholder used was a cross baffle of approximately 30% blockage. Provision was made for the adjustment of the flameholder with respect to the burner exit and source position. This adjustment was accomplished by means of a micrometer screw located outside the sandbagged area. Two burner heads, which differed only in their length, were provided. The difference in length of the two heads was the length of the source ($1\frac{3}{16}$ inches). Prior to isolation of the system, the flameholder was adjusted to a position 3-inches from the exit of the longer head (i.e., at the upper edge of the source). By adjustment of the head screw it was then possible to vary the flameholder-exit position to any desired value. The diameter of the burner was $\frac{1}{2}$ inches.

The source was a hollow cylinder fabricated from a gold tube $\frac{1}{2}$ -inch I.D. and 0.006 inch thick. Copper was plated on the outside to increase the strength.

* Calculation of shielding requirements were performed by Mr. J. V. Nehemias of the University of Michigan's Fission Products Laboratory, and Mr. A. H. Emmons of the University's Radiological Safety Department. Their assistance in the design of the equipment is gratefully acknowledged.

Procedure

To obtain data to show possible changes in combustion processes due to radiation, simple experimental techniques were utilized. These consisted of the measurement of flame speeds in the Bunsen burner, blow off velocities from a spherical flameholder, and pressure drop due to combustion in the constant area combustor.

The various burners were ignited by means of a spark discharge from an induction coil. Flow rates were then adjusted to the lowest value for which the flame remained stable and the measurements taken. The flow rate was increased, until the flame blew out, with data being recorded as the flow rate increased.

The following data were obtained for the Bunsen flames:

- 1) Flow rate
- 2) Ambient Pressure
- 3) Burner Size (diameter)
- 4) Fuel/air ratio (constant)
- 5) A photograph of the flame
- 6) Type of fuel (propane only).

For blow off velocities the following data were recorded:

- 1) Flow rate
- 2) Burner (jet) diameter
- 3) Fuel/air ratio
- 4) Activity
- 5) Type of fuel
- 6) Ambient Pressure.

For the constant area combustor, the following data were obtained:

- 1) Flow rate
- 2) Pressure drop due to burning
- 3) Cold Drag (from calibration)
- 4) Fuel-air ratio (variable)
- 5) Activity
- 6) Flameholder position relative to source
- 7) Burner length
- 8) Type of fuel (propane or ethylene)
- 9) Ambient pressure.

Results

Comparison of the flame speed and the blow off velocities from a spherical flameholder for propane-air flame, showed no significant changes due to radiation. Some of these data are presented in Figures 13 and 14.

In the constant area combustion, the effect of the radiation tended to increase the pressure drop due to burning as a function of fuel-air ratio above the pressure drop when no radiation was present. These results are shown in Figures 15 through 25. For propane-air, these results are expressed in terms of the air specific impulse, which is defined as

$$S_a = \frac{F_2}{W_A \phi(M)} \quad (10)$$

where F_2 is the force on the burned gas, W_A is the air flow rate and $\phi(M)$ is a function of the Mach number of the exit gases. This equation is a measure of the overall effectiveness of heat addition to a moving stream (8,9).

These data (constant area combustor) are for one atmosphere exit pressure and source activities of 2050 to 8 curies. Mass velocity is a parameter for each curve. The flameholder position for activities of 2050 and 2000 curies was at the downstream end of the source and for 1800 and 1250 curies at the upstream end of the source.

In addition to these data obtained at varying fuel-air ratios, considerable data were obtained for 0.067 propane-air at mass velocities (G) of .75 lb per sec-ft² to $G = 5$. This choice of operating range proved to be unfortunate since examination of the data for propane-air (Fig. 15-25) shows that for this range of mass velocities the effect of the radiation is very slight.

Quantitatively, there appeared to be slight variations in the rich and lean blow-off limits. No attempts were made to measure ignition limits.

Discussion

The results of this experimental work are readily analyzed from consideration of the ratio of reaction rate constants given by equation (4) and the active fraction given by equation (9a) or (9b).

The molal flow rate for most of this work was in the range of 10^{-3} - 10^{-4} mols per second and the value of θ is about 10^{-2} for Bunsen flames and 10^{-1} for the spherically stabilized flame and ram jet type combustor. Substituting these values in equation (9b) gives an order of magnitude of $\frac{Y(\beta)}{\beta}$ of 10^{-4} to 10^{-6} active molecules per molecule per curie of activity. Since the activity for the spherically stabilized flame and the Bunsen flame never exceeded 100 curies, and for the constant area combustor was in excess of 1,000 curies, $Y(\beta)$ is therefore in the range 10^{-4} to 10^{-1} . These values are tabulated in Table II

TABLE II

	$Y(\beta)$	$\beta(\text{curies})$	$Y(\beta)/\beta$	k^1/k
*Bunsen Flame	10^{-3}	100	10^{-5}	1.001
*Spherically Stabilized Flame	10^{-4}	100	10^{-6}	negligable
**Constant Area Combustor	10^{-1}	2000	10^{-4}	1.1

* For primary radiation only.

** Includes factor for secondary radiation.

The very low values for the spherically stabilized flame are due to the low value of $\frac{L}{R}$ in equation (9b).

The temperatures of about 500°K exp (E_T/RT) would have values in the range of 1-10 (i.e. $E_T \approx 1-10$ K cal.) And k^1/k would vary from one to a maximum of about two. It is therefore seen that the radiation will cause increased reaction rates in the combustor. This analysis is predicated on the mechanism of reaction remaining fixed. It is possible, however, that the active specie introduced may alter the course of the reaction and initiate other reactions. The actual course of the observed effect is more likely to be a combination of increased reaction ratio and modified mechanisms.

It is interesting to note that the rate of energy addition into the system due to radiation is very small, being approximately 10 joules per hour.

Conclusion

Beta radiation will increase the pressure drop due to combustion in a constant area chamber. The data should be considered as applicable only to the experimental systems considered and no quantitative conclusions should be drawn for other systems.

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